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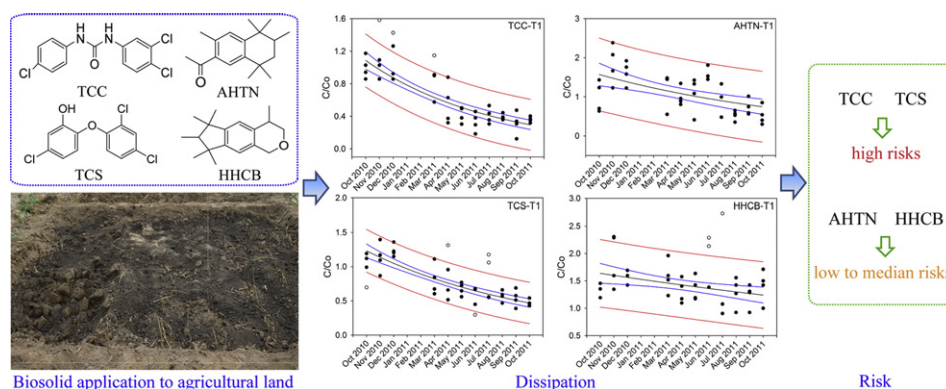
## Science of the Total Environment

journal homepage: [www.elsevier.com/locate/scitotenv](http://www.elsevier.com/locate/scitotenv)Field dissipation and risk assessment of typical personal care products  
TCC, TCS, AHTN and HHCB in biosolid-amended soilsFeng Chen <sup>a,b</sup>, Guang-Guo Ying <sup>a,\*</sup>, Yi-Bing Ma <sup>c</sup>, Zhi-Feng Chen <sup>a</sup>, Hua-Jie Lai <sup>a</sup>, Feng-Jiao Peng <sup>a</sup><sup>a</sup> State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China<sup>b</sup> Guizhou Academy of Environmental Science and Designing, Guizhou 550002, China<sup>c</sup> Ministry of Agriculture Key Laboratory of Plant Nutrition and Nutrient Cycling, Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences, Beijing 100081, China

## HIGHLIGHTS

- Four personal care products were detected in biosolid-amended soils.
- The concentration order in the three sites: TCC > TCS > AHTN > HHCB.
- The four compounds persisted with dissipation half-lives of 51–900 days.
- High risks are expected for TCC and TCS, but low–medium risks for AHTN and HHCB.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The antimicrobial agents triclorocarban (TCC) and triclosan (TCS) and synthetic musks AHTN (Tonalide) and HHCB (Galaxolide) are widely used in many personal care products. These compounds may release into the soil environment through biosolid application to agricultural land and potentially affect soil organisms. This paper aimed to investigate accumulation, dissipation and potential risks of TCC, TCS, AHTN and HHCB in biosolid-amended soils of the three field trial sites (Zhejiang, Hunan and Shandong) with three treatments (CK: control without biosolid application, T1: single biosolid application, T2: repeated biosolid application every year). The one-year monitoring results showed that biosolids application could lead to accumulation of these four chemicals in the biosolid-amended soils, with the residual concentrations in the following order: TCC > TCS > AHTN > HHCB. Dissipation of TCC, TCS, AHTN and HHCB in the biosolid-amended soils followed the first-order kinetics model. Half-lives for TCC, TCS, AHTN and HHCB under the field conditions of Shandong site were 191, 258, 336 and 900 days for T1, and 51, 106, 159 and 83 days for T2, respectively. Repeated applications of biosolid led to accumulation of these personal care products and result in higher ecological risks. Based on the residual levels in the trial sites and limited toxicity data, high risks to soil organisms are expected for TCC and TCS, while low-medium risks for AHTN and HHCB.

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## 1. Introduction

As an alternative to landfilling and ocean disposal, application of municipal biosolids to agricultural land is becoming increasingly popular. Biosolids applied to farmland can bring some benefits, such as improving soil properties, and supplying nutrients essential for plant growth including nitrogen, phosphorous and other essential micronutrients such as nickel, zinc and copper (Kimberley et al., 2004; USEPA, 2000). Land application of biosolids has become a common practice throughout the world. However, concerns continue to be raised about the potential risks of this practice to the soil environment and public health, because biosolids contain a broad range of toxic inorganic and organic contaminants (Kinney et al., 2006; Oleszczuk and Baran, 2004).

The United States Environmental Protection Agency developed standards for biosolids (USEPA, 1995), in which the upper limit values for pathogens and heavy metals such as arsenic, chromium, and nickel were mentioned. In 1984, China proposed controlling standards for contaminants in biosolids applied to farmland, which mainly focus on heavy metals (China EPA, 1988). The controlling standards do not include the maximum allowable concentrations of organic pollutants, except benzo(a)pyrene (China EPA, 1988). Many previous studies have investigated heavy metals (Speir et al., 2003; Zufiaurre et al., 1998) and some persistent organic contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in biosolids (Ahmad et al., 2004; Al-Rashdan et al., 2010) and biosolid-applied soils (Baran and Oleszczuk, 2003; Oleszczuk and Baran, 2004). Only very limited studies have reported the detection of personal care products in biosolid-amended soils, for example, in Ohio, USA (Wu et al., 2010), Mississippi, USA (Xia et al., 2010), and Ontario, Canada (Yang and Metcalfe, 2006). So far, little is known about the field dissipation of personal care products in biosolid-amended soils and potential risks to terrestrial organisms. This has also seriously hampered the development of relevant environmental standards.

It is known that the antibacterial agents triclocarban (TCC) and triclosan (TCS), and synthetic musks AHTN (Tonalide) and HHCB (Galaxolide) are extensively used in many household and personal care products (Amorim et al., 2010; Balk and Ford, 1999). These personal care products could enter the terrestrial environment through biosolid application to agricultural land (USEPA, 2000; Xia et al., 2010). A few studies have investigated the degradation of personal care products such as TCS in biosolid-amended soils under laboratory or greenhouse conditions and short-period field conditions (Langdon et al., 2011; Wu et al., 2009). However, there have been few systematic field studies on the accumulation, dissipation and risks of personal care products in soils amended with biosolids. Moreover, the dissipation of organic contaminants under field conditions could be very different to that under laboratory conditions.

The aims of this study were to evaluate contamination levels of four common personal care products (TCC, TCS, AHTN and HHCB) in biosolids and biosolid-amended soils of three field trial sites (Zhejiang, Hunan and Shandong), investigate their dissipation patterns in the biosolid-amended soils under different treatments (T1: single application; T2: repeated applications), and assess their potential risks to soil organisms. The results from this study can help evaluate the environmental impacts of these personal care products associated with biosolid application on agricultural land.

## 2. Materials and methods

### 2.1. Chemicals and materials

Triclocarban (TCC), Triclosan (TCS), Galaxolide (HHCB) and internal standard AHTN-d3 for AHTN and HHCB were purchased from Dr. Ehrenstorfer GmbH (Germany), while Tonalide (AHTN) was obtained

**Table 1**

Chemical structures and properties of personal care products investigated in this study.

Compounds	Chemical structure	Chemical properties
Triclocarban (TCC)		CAS No: 101-20-2 M.W.: 315.58 LogK <sub>ow</sub> : 4.9 <sup>c</sup> K <sub>oc</sub> (L/kg): 50118 <sup>c</sup> Half-life (days) in soil: 108 <sup>c</sup> Water solubility (mg/L at 20 °C): 0.6479 <sup>c</sup> Use: antiseptic and disinfectant
Triclosan (TCS)		CAS No: 3380-34-5 M.W.: 289.54 LogK <sub>ow</sub> <sup>a</sup> : 4.7 <sup>c</sup> K <sub>oc</sub> (L/kg) <sup>b</sup> : 18408 <sup>c</sup> Half-life (days) in soil: 18 <sup>c</sup> Water solubility (mg/L at 20 °C): 4.621 <sup>c</sup> Use: antiseptic and disinfectant
Tonalide (AHTN)		CAS No: 1506-02-1 M.W.: 258.4 LogK <sub>ow</sub> : 5.2 <sup>d</sup> K <sub>oc</sub> (L/kg): 4800–13600 <sup>e</sup> Water solubility (mg/L at 20 °C): 1.8 <sup>d</sup> Use: essence
Galaxolide (HHCB)		CAS No: 1222-05-5 M.W.: 258.4 LogK <sub>ow</sub> : 5.9 <sup>d</sup> K <sub>oc</sub> (L/kg): 4200–7900 <sup>e</sup> Water solubility (mg/L at 20 °C): 1.75 <sup>d</sup> Use: essence

<sup>a</sup> K<sub>ow</sub>: n-octanol-water partitioning coefficient (Ying and Kookana, 2005).

<sup>b</sup> K<sub>oc</sub>: sorption coefficient (Ying et al., 2003).

<sup>c</sup> Data from Ying et al. (2007).

<sup>d</sup> Data from Moeder et al. (2010).

<sup>e</sup> Data from Litz et al. (2007).

from TRC (Canada). The internal standards <sup>13</sup>C<sub>12</sub>-TCS for TCS and TCC-d7 for TCC were purchased from Cambridge Isotope Laboratories Inc. (Massachusetts, USA). The chemical structures and properties of the four target compounds are given in Table 1. All the organic solvents were HPLC grade and purchased from Merck Corporation (Shanghai, China). Ultrapure water was supplied by a Milli-Q system from Millipore (Watford, UK). Glass wool (CNW, Canada) and sodium sulfate were baked at 400 °C for 4 h and preserved in a desiccator. Silica gel (100–200 mesh for TCC and TCS, 80–100 mesh for AHTN and HHCB) and neutral alumina were sequentially Soxhlet extracted with methanol and dichloromethane for 24 h prior to use, then baked at 160 °C for 24 h and stored in a sealed desiccator. All glassware was hand-washed with detergent and tap water, rinsed with Milli-Q water, and then baked at 400 °C for 4 h.

Individual stock solutions of the target analytes and internal standards were prepared at 100 mg/L in methanol and stored in amber glass bottles at −18 °C. Composite working solutions at the desired concentrations were made by appropriate dilution of the individual stock solutions.

### 2.2. Field trials

The field trials were conducted at three sites Zhejiang (ZJ), Hunan (HN) and Shandong (SD) in China. Three treatments at each site were established: the controls without application of biosolid (CK), one biosolid application (T1) and repeated application every year (T2). Each treatment had four replicate plots (3 × 2 m, each). The biosolid used for the field experiments was obtained from Beijing centralized sludge treatment plant, which treats 70% of sludge from domestic wastewater treatment plants in Beijing. For T1, the biosolid was applied at the three

sites only on the 31st May 2007 at a rate of 60 t/ha, while for T2, biosolid was first applied at a rate of 60 t/ha on the 31st May 2007, and then the same amount of biosolid was applied on each 5th October following the first application till October 2010. The biosolid was mixed with a surface soil layer up to a depth of 20 cm. Three applications were carried out for T2 until soil samples were collected from the three trial sites in October 2010.

Initial field trials only focused on inorganic contaminants in the biosolid-amended soils (Li et al., 2012). Surface biosolid amended soil samples (0–20 cm) were collected on October 5, 2010 for the first time prior to the re-application of biosolid for analysis of organic contaminants in this study, and then once a month till October 2011. An exception was in January and February 2011, when sampling campaign was not carried out because of the freezing weather in the Shandong site. After the first sampling, Zhejiang and Hunan trial sites were closed down due to the logistic problem in transport of the biosolid. Soil samples were collected in 1 L glass jars from each field plot at the depth of 0–20 cm from five points in each plot and then combined into one composite sample. The collected soil samples and biosolid samples were freeze-dried, then sieved through a 0.90 mm mesh standard screen and then stored in the dark at 4 °C prior to extraction.

Information about the properties of soils from the field trial sites are presented in Table 2. The annual temperatures for Zhejiang, Hunan and Shandong were 15.9, 19.1 and 12.9 °C; while the annual rainfalls for these three sites were 1168, 1360 and 522 mm, respectively. Soil pH was determined with 0.01 M CaCl<sub>2</sub> (soil to solution ratio of 1:5) using a pH meter, while soil particle size distribution was analyzed by using the pipette method mentioned in our previous study (Chen et al., 2011). Organic carbon content (OC) of soils was measured by a LECO carbon and nitrogen analyzer.

## 2.3. Extraction

### 2.3.1. Extraction and cleanup of TCC and TCS

TCC and TCS were extracted from soils and biosolids using our previously published method (Chen et al., 2011) (Fig. S1). After being spiked with 100 µg/kg of each internal standard (TCC-d7, and <sup>13</sup>C<sub>12</sub>-TCS), all samples (5.0 g soil and 0.5 g biosolid dry weight) were extracted by ultrasonication using 10 mL of ethyl acetate at room temperature for three times (15 min each time). The extracts were combined and concentrated to nearly dryness under a gentle nitrogen stream. Further cleanup was performed by self-made silica gel cartridges (each 18 cm × 1 cm i.d.), which consisted of glass wool (CNW) (bottom), silica gel (1 g) and anhydrous sodium sulfate (about 0.5 cm) (top) in each cartridge. The extracts (redissolved in 1 mL of n-hexane) were then purified by the silica gel cartridges, which were preconditioned sequentially with methanol (4 mL), ethyl acetate (4 mL) and n-hexane (6 mL). The extracts were passed through the preconditioned silica gel cartridges, and then sequentially eluted by 6 mL each of n-hexane, ethyl

acetate and methanol. The last two eluates were collected and dried under a gentle stream of nitrogen gas. The final extracts were re-dissolved in 1 mL methanol and passed through a nylon filter (13 mm × 0.22 µm, Anpu, Shanghai) into 2 mL amber glass vials, and stored at –18 °C until analysis.

### 2.3.2. Extraction and cleanup of AHTN and HHCB

Extraction procedure was optimized from previous studies (Tao et al., 2002; Liu et al., 2011). The soil and biosolid samples were freeze-dried and extracted using an Accelerated Solvent Extractor (Dionex ASE 300) equipped with 34 mL stainless steel extraction cells (Fig. S1). One cellulose filter followed by in-cell cleanup sorbents was placed at the bottom of each cell. The sorbents consisted of 2.0 g of silica and 2.0 g of neutral aluminum from bottom to top. The corresponding amount of each soil or biosolid sample (5.0 g for soil, or 0.5 g for biosolid) was placed into the cells and then spiked with 100 ng of the internal standard AHTN-d3. After this, the cells were mixed well and kept in the dark at 4 °C overnight. After loading 5 g of sodium sulfate, the remaining volume in each cell was filled with quartz sand. The optimized extraction conditions were given as follows: the extraction solvent, acetone-dichloromethane (1:1, v/v); extraction temperature, 140 °C; heat-up time, 5 min; static cycles, 2; static time, 5 min. The flush volume amounted to 60% of the extraction cell volume. The extracted analytes were purged from the sample cell using pressurized high purity nitrogen for 1 min. The extracts were concentrated to about 5 mL by a rotary evaporator at 30 °C, and then under a gentle stream of nitrogen gas to near dryness. The extracts were re-dissolved in 1 mL of hexane, and then filtered through nylon filters (13 mm × 0.22 µm, Anpu, Shanghai) to 2 mL amber glass vials. The final extracts were stored at –18 °C until analysis.

## 2.4. Instrumental analysis

### 2.4.1. LC-MS/MS

The target compounds TCC and TCS in the extracts were determined using an Agilent 1200 rapid resolution liquid chromatography coupled to an Agilent G6460A triple quadrupole mass spectrometer (RRLC-MS/MS) with electrospray ionization (ESI). The chromatographic separation was performed on an Agilent SB-C18 column (3.0 mm × 100 mm ID, 1.8 µm particle size) with an RRLC in-line pre-column filter (4.6 mm, 0.2 µm filter). The column temperature was maintained at 40 °C, and the injection volume was 10 µL. The mobile phase was Milli-Q water (A) and acetonitrile (B), at a flow rate of 0.3 mL/min. The gradient elution started with 40% B, increased to 70% B at 15 min, and to 95% B at 20 min and kept at 95% B for 2 min, then returned to the initial 40% B for column re-equilibration (5 min).

Multiple reaction monitoring (MRM) in ESI negative mode was used in the quantitative analysis (Table S1). Collision energy (CE), fragmentor voltage, and MRM transitions for each compound were

**Table 2**  
Information of the field trial sites and treatments.

Treatment <sup>a</sup>	Crops	Soil type/texture	Soil moisture	pH <sup>b</sup>	OC % <sup>c</sup>	Sand % (>0.063 mm)	Coarse sand % (0.02–0.063 mm)	Silt % (0.002–0.02 mm)	Clay % (<0.002 mm)	Biosolid application (t/ha)
ZJ-CK	Rice and rape	Paddy soil/silt loam	100	6.3 ± 0.5	1.4 ± 0.4	23.5 ± 6.7	14.9 ± 10.0	51.8 ± 7.4	9.7 ± 9.2	0
ZJ-T1				6.8 ± 0.2	2.1 ± 0.6	19.1 ± 5.1	17.5 ± 9.8	52.2 ± 3.7	11.2 ± 6.8	60 once
ZJ-T2				7.1 ± 0.1	1.2 ± 0.2	36.2 ± 4.3	14.0 ± 5.8	40.1 ± 2.7	9.7 ± 1.0	60 every year
HN-CK	Wheat and maize	Red soil/loam	24–25	4.3 ± 0.1	1.0 ± 0.1	23.9 ± 9.3	22.9 ± 3.9	42.9 ± 10.6	10.3 ± 1.7	0
HN-T1				5.6 ± 0.1	1.3 ± 0.1	27.4 ± 6.0	20.8 ± 3.2	42.2 ± 7.3	9.7 ± 1.0	60 once
HN-T2				7.0 ± 0.2	2.4 ± 0.2	30.0 ± 6.5	15.6 ± 3.9	47.6 ± 8.1	7.4 ± 3.5	60 every year
SD-CK	Wheat and maize	Fluvo-aquic soil/clay loam	23	7.6 ± 0.2	0.6 ± 0.0	9.8 ± 4.0	28.8 ± 9.9	39.7 ± 2.7	21.7 ± 4.2	0
SD-T1				7.6 ± 0.1	1.0 ± 0.1	8.0 ± 2.5	23.6 ± 6.6	46.5 ± 6.3	21.9 ± 1.5	60 once
SD-T2				7.5 ± 0.1	1.4 ± 0.3	13.5 ± 3.8	21.4 ± 3.7	39.1 ± 1.3	26.0 ± 0.8	60 every year

<sup>a</sup> The treatments at each site include control (CK), treatment 1 (T1), and treatment 2 (T2); ZJ: Zhejiang, HN: Hunan, SD: Shandong.

<sup>b</sup> Mean ± standard deviation (%) (n = 4). All the pH, OC, sand, coarse sand, silt and clay content values were detected in the samples collected in October 2010.

<sup>c</sup> OC: organic carbon content.

optimized by Optimizer (Agilent, Palo Alto, USA). The following optimized ESI parameters were applied: drying gas ( $N_2$ ) flow rate 6 mL/min, dry gas temperature 350 °C, nebulizing gas ( $N_2$ ) pressure 50 psi, capillary voltage 3500 V, sheath gas temperature 350 °C and sheath gas flow rate 12 mL/min. Detailed mass spectrometric operating conditions could be found in [Chen et al. \(2010\)](#).

#### 2.4.2. GC-EI-MS

The target compounds AHTN and HHCb in the extracts were determined using an Agilent 6890 N GC interfaced to a 5975B MSD (GC-MS), equipped with a DB-5MS column (30 m  $\times$  0.25 mm i.d., 0.25  $\mu$ m film thickness, J&W Scientific Co., USA). Analyses were operated in selected ion monitoring (SIM) mode following electron-impact ionization (EI) (Table S1). The temperatures for the GC-MS interface, ion source and quadrupole were 280 °C, 250 °C and 150 °C, respectively. The helium (purity > 99.999%) was used as carrier gas at a constant flow of 1.0 mL/min. Each extract sample (2  $\mu$ L) was injected in pulsed splitless mode. The injector temperature was set at 280 °C. The GC oven temperature was programmed as follows: 80 °C for 0 min, increased to 170 °C at 15 °C/min, from 170 °C to 185 °C at 1 °C/min, then to 300 °C at a rate of 20 °C/min for 5 min.

#### 2.5. Quality assurance and quality control

Reagent blank, method blank and spiked matrix were analyzed together with the biosolid and soil samples. None of the four target compounds were detected in the blank soils. The recovery experiments were performed by spiking a known concentration of each target compound (100  $\mu$ g/kg) into soil samples. Satisfactory performance in regards to recovery and limits of detection (LOD) and quantitation (LOQ) was obtained and is shown in Table S2. The LOD and LOQ were determined by calculating signal-to-noise (S/N) ratios of 3 and 10, respectively, which were obtained from analysis of those soil samples spiked at low concentrations. The recoveries for the four target compounds ranged from 95% to 115%, and their LOQs ranged between 0.39 and 1.58  $\mu$ g/kg.

#### 2.6. Statistical analysis and risk assessment

Analysis for significant differences ( $p < 0.05$ ) between the concentration data of the target compounds in three different type soils and different treatments was performed using SPSS 20 (IBM, New York). A univariate analysis of variance (ANOVA) and paired sample statistics were applied. Prior to nonlinear regression fitting, the detected concentration data at each sampling time were converted to a ratio of the initial concentration ( $C/C_0$ ).  $C$  was the concentration of a target compound at time  $t$ .  $C_0$  showed the average of the initial value. A first-order degradation model with two fitting parameters was applied to fit the concentration data. The first-order rate constant ( $k$ ) was obtained from the formula ( $C = C_0 * \exp(-k * t)$ ), while half-lives ( $t_{1/2}$ ) were calculated using the first-order rate constant ( $k$ ) in the formula ( $t_{1/2} = 0.693/k$ ).

A risk quotient (RQ) approach was applied to evaluate potential ecological risks of the target compounds according to the ecological risk assessment guidelines ([European Commission, 2003](#)). RQ values were calculated from the measured environmental concentration (MEC) and predicted no effect concentration (PNEC) of each compound. PNEC was calculated based on terrestrial toxicity data reported in the literature, in combination with the corresponding assessment factor (AF). RQ levels were identified by the standard reported in [Hernando et al. \(2006\)](#):  $RQ < 0.1$ , low risk;  $0.1 \leq RQ < 1$ , medium risk;  $RQ \geq 1$ , high risk.

### 3. Results

#### 3.1. Levels of personal care products in the biosolid

All of the four common personal care products TCC, TCS, AHTN and HHCb were detected in the biosolid from Beijing sludge treatment plant, with their concentrations of 34,900  $\mu$ g/kg, 3470  $\mu$ g/kg, 1400  $\mu$ g/kg and 2950  $\mu$ g/kg, respectively. Compared to the levels reported worldwide, the concentrations of these four target compounds were in the lower end of the concentration ranges reported ([Table 3](#)). The highest concentrations for TCC and TCS were reported in the biosolids from the United States (48,100  $\mu$ g/kg and 19,700  $\mu$ g/kg) ([McClellan and Halden, 2010](#); [Snyder et al., 2010a](#)). The highest concentrations for AHTN and

**Table 3**

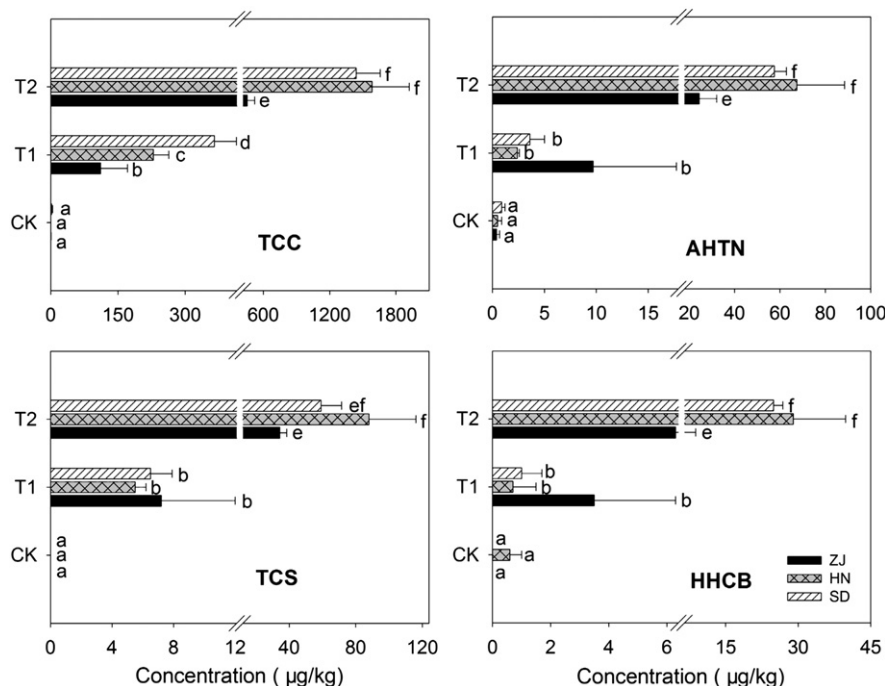
Comparison of concentrations of the personal care products in biosolids and soils ( $\mu$ g/kg).

Location	TCC	TCS	AHTN	HHCb	References
<i>Biosolids</i>					
China	34882	3473	1400 54–169284 475–13900	2950 82–703681 3580–78600	This study <a href="#">Zeng et al., 2005</a> <a href="#">Shek et al., 2008</a> <a href="#">Gatidou et al., 2007</a>
Greece		1840			<a href="#">Müller et al., 2006</a>
Germany			1100–4200	2900–10400	<a href="#">Yu and Wu, 2012</a>
USA	48100 (36960) <sup>a</sup> 4890–9280 6000–40000	271.9–1965 19700(12640) <sup>a</sup> 90–7060			<a href="#">McClellan and Halden, 2010</a> <a href="#">Cha and Cupples, 2009</a> <a href="#">Snyder et al., 2010a</a>
UK			120–16000 (4700)	1900–81000 (27000) <sup>b</sup>	<a href="#">Stevens et al., 2002</a>
Australia		90–16790 (2320) <sup>b</sup>			<a href="#">Ying and Kookana, 2007</a>
Spain		1300–1490			<a href="#">Nieto et al., 2009</a>
Canada			1040.2–1569.0 (1349.4) <sup>b</sup>	5772.7–7896.7 (6788.4) <sup>b</sup>	<a href="#">Yang and Metcalfe, 2006</a>
Switzerland	4740	8030	741–4161	2293–12157	<a href="#">Al-Rajab et al., 2009</a> <a href="#">Herren and Berset, 2000</a>
<i>Soils</i>					
China	111–1584	5.5–87.9	2.4–67.5	0.7–29.0	This study
Mexico		4.4–18.6			<a href="#">Durán-Alvarez et al., 2009</a>
USA	1.20–65.10 1.4–2.4	<LOD-1.02 ND			<a href="#">Cha and Cupples, 2009</a> <a href="#">Wu et al., 2010</a>

<sup>a</sup> Maximum concentration and mean concentration within parentheses.

<sup>b</sup> Mean concentration in parentheses.





**Fig. 1.** Concentrations of TCC, TCS, AHTN and HHCB in the soils collected from the three trial sites Zhejiang (ZJ), Hunan (HN) and Shandong (SD) in October 2010. CK, T1 and T2 represent control, treatment 1 with one biosolid application, and treatment 2 with biosolid application every year. Letters (a, b, c, d, e and f) indicate the significant difference of concentration data by Duncan's multiple range test for each compound among the three sites ( $p < 0.05$ ). Error bars represent standard deviations of the measured concentrations.

HHCB were found in the biosolids from Guangzhou, China (169,000  $\mu\text{g/kg}$  and 704,000  $\mu\text{g/kg}$ ) (Zeng et al., 2005), which are 10 times those from the present study. Such large differences in their levels are most probably due to the different usages and treatment technologies used in wastewater treatment plants and final sludge digestion plants. The biosolid used in the field application in the present study has been digested and dried before application, which may influence the levels of organic contaminants in the final biosolid.

### 3.2. Occurrence of personal care products in the soils of the three field trial sites

The four target compounds (TCC, TCS, AHTN and HHCB) were detected in all biosolid-amended soils from the three trial sites (HN, SD and ZJ) in October 2010, as shown in Fig. 1 and Table S3. No or trace amounts of these compounds were detected in the soils from the control plots without application of biosolid. The concentrations for these four compounds in the biosolid-amended soils of T2 treatment (repeated biosolid applications) were significantly higher than those of T1 (single biosolid application) ( $p < 0.05$ ).

The concentration levels for the four compounds of both T1 and T2 in the biosolid-amended soils of the three sites were found to have the following order: TCC > TCS > AHTN > HHCB (Table S3 and Fig. 1). TCC was found to have concentrations ranging from 111 (ZJ) to 365 (SD)  $\mu\text{g/kg}$  for T1, and from 454 (ZJ) to 1584 (HN)  $\mu\text{g/kg}$  for T2. TCS ranged from 5.5 (HN) to 7.2 (ZJ)  $\mu\text{g/kg}$  for T1 and from 34.3 (ZJ) to 87.9 (HN)  $\mu\text{g/kg}$  for T2. AHTN was found at concentrations of 2.4 (HN)–9.7 (ZJ)  $\mu\text{g/kg}$  for T1 and 24.4 (ZJ)–67.5 (HN)  $\mu\text{g/kg}$  for T2, while HHCB was found at 0.7 (HN)–3.5 (ZJ)  $\mu\text{g/kg}$  for T1 and 6.3 (ZJ)–29.0 (HN)  $\mu\text{g/kg}$  for T2. It is noted that the four target compounds under T2 showed the following order of concentration levels in the three sites: HN > SD > ZJ, which may be related to the influences of different site soil and climatic conditions (Table 2). No significant differences among the three sites were found for the four target compounds under T1 except for TCC having the lowest concentrations at the ZJ site (Fig. 1). The paddy soils at the ZJ site had higher moisture contents than the other two sites, which

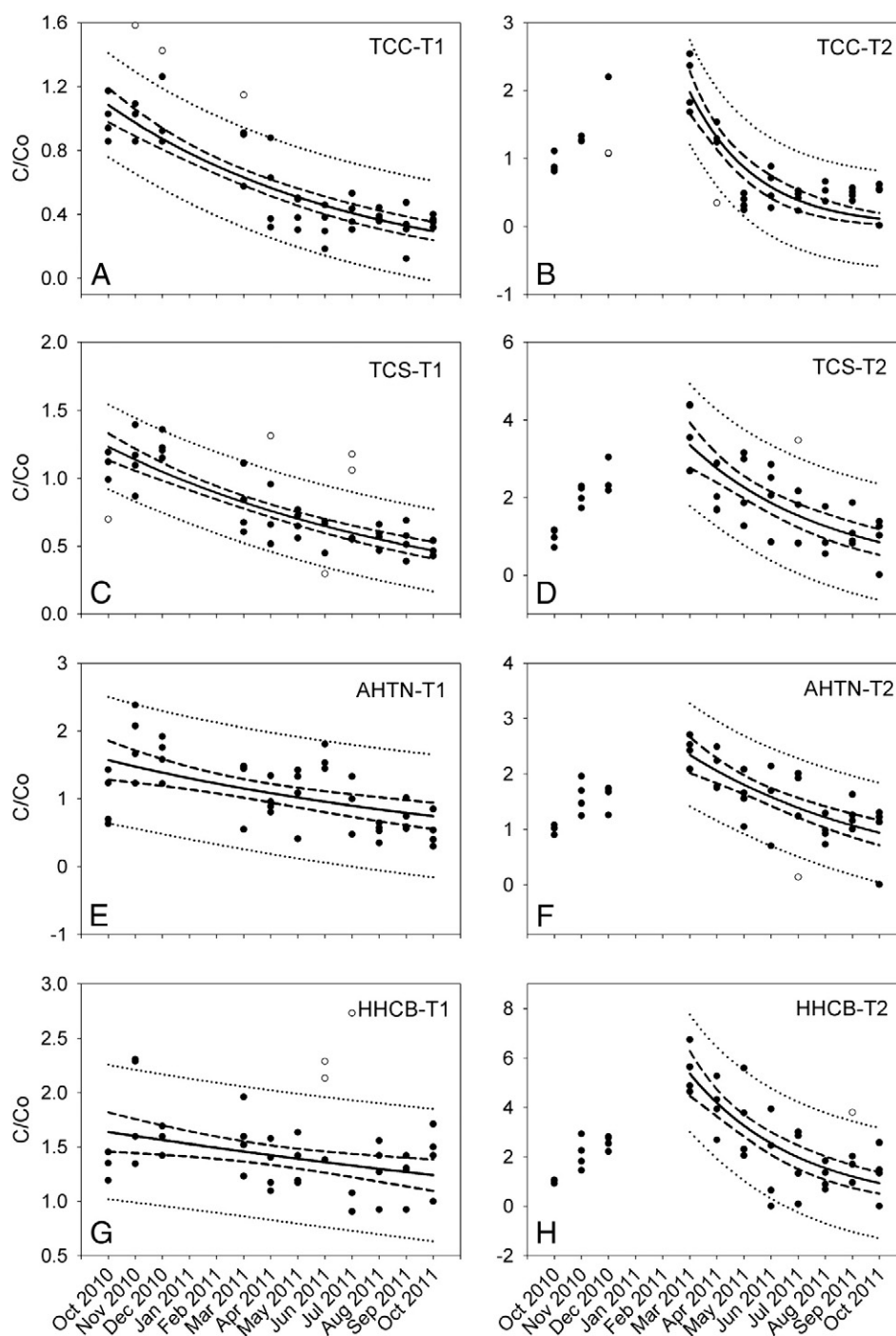
may enhance microbial degradation of the chemicals from the newly applied biosolid.

### 3.3. Field dissipation in the biosolid-amended soils

Field dissipation of the four personal care products was assessed at the SD site for one year from October 2010 to October 2011. Their dissipation curves are shown in Fig. 2, with measured concentrations for each compound within one year being given in Table S4. For T1, significant dissipation was found for the four target compounds in the soils. But for T2, wide variations in their concentrations were found from October to December, resulting from inhomogeneous soil conditions after reapplication of biosolid during the frosty period. The big variations observed during the period were also reported in previous studies (Baran and Oleszczuk, 2003; Langdon et al., 2012). Thus kinetic fitting was performed only for the later period from March 2010 to October 2011. Dissipation of the four target compounds in the soils of T1 and T2 treatments followed the first-order kinetic model (Fig. 2). The dissipation half-lives of TCC, TCS, AHTN and HHCB were found to be much higher for T1 (191, 258, 336 and 900 days) than for T2 (51, 106, 159 and 83 days) (Table 4).

## 4. Discussion

The field trials at the three sites (ZJ, HN and SD) showed presence and persistence of the four common personal care products (TCC, TCS, AHTN and HHCB) in the biosolid-amended soils under both treatments (T1: one application; T2: repeated applications) (Fig. 1). In contrast, no or trace detection was found in the control plots without application of biosolid. This suggests the occurrence of the four target compounds in the biosolid-amended soils is due to the application of biosolid. Similar results for the two antimicrobials TCC and TCS were reported in Michigan soils more than one year after biosolid application, with the highest concentrations of 65.1 and 1.02  $\mu\text{g/kg}$ , respectively (Cha and Cupples, 2009). To our knowledge, our data represent the first field report of the two polycyclic musks (AHTN and HHCB) in biosolid-amended agricultural soils.



**Fig. 2.** Field dissipation of TCC, TCS, AHTN and HHCB in the biosolid-amended soils of the Shandong site within one year (October 2010 to October 2011). All concentration data are normalized as a ratio of the concentration at each sampling time to the initial concentration ( $C/C_0$ ). Data points with empty symbols are treated as outliers during data fitting since the points are not included between the two 95% prediction bands. The nonlinear regression fits for the first-order kinetic model, 95% confidence band and 95% prediction band are represented by the solid line, dash line and dotted line, respectively. A: TCC for T1, B: TCC for T2; C: TCS for T1, D: TCS for T2; E: AHTN for T1, F: AHTN for T2; G: HHCB for T1, H: HHCB for T2.

The detection of the four personal care products in the three field trial sites (HN, SD and ZJ) in October 2010 since first application of biosolid in May 2007 suggests their persistence in the soils. With the SD site as an example, we calculated the input amounts of the four chemicals based on the application rates of biosolid, and compared with the measured concentrations in the biosolid-amended soils in October 2010. Comparing the measured concentrations with the predicted concentrations, we could conclude that dissipation of the four chemicals in the soils did occur following biosolid application

(Table 5). One year field monitoring at the SD site further demonstrated that the four chemicals (TCC, TCS, AHTN and HHCB) in the biosolid-amended agricultural soils dissipated slowly with half-lives ranging between 51 days and 900 days (Table 4). The half-lives of the four chemicals in the soils under one biosolid application (T1) were found much higher than under repeated applications (T2), most likely due to aging effects of chemicals (Bogan and Sullivan, 2003). The increase of contact time could lead to increase the sequestration and reduce the availability of compound for the biodegradation. On the other hand, a

**Table 4**

First-order degradation rate constants and correlation coefficients for the personal care products in the biosolid-amended soils of the Shandong site.

Compound	Calculation	T1	T2
TCC	Fitting formula	$Y = 1.2097 * \exp(-0.1084 * X)$	$Y = 22.8805 * \exp(-0.4083 * X)$
	R <sup>2a</sup>	0.7511	0.7191
	p-value <sup>b</sup>	<0.0001	<0.0001
	k (error) <sup>c</sup>	0.1084 (0.0103)	0.4083 (0.0562)
	t <sub>1/2</sub> (error) <sup>d</sup>	191 (18)	51 (7)
TCS	Fitting formula	$Y = 1.3346 * \exp(-0.0805 * X)$	$Y = 10.8496 * \exp(-0.1956 * X)$
	R <sup>2</sup>	0.7570	0.5858
	p-value	<0.0001	<0.0001
	k (error)	0.0805 (0.0073)	0.1956 (0.0336)
	t <sub>1/2</sub> (error)	258 (23)	106 (18)
AHTN	Fitting formula	$Y = 1.6714 * \exp(-0.0619 * X)$	$Y = 5.1286 * \exp(-0.1305 * X)$
	R <sup>2</sup>	0.3125	0.5657
	p-value	0.0001	<0.0001
	k (error)	0.0619 (0.0153)	0.1305 (0.0225)
	t <sub>1/2</sub> (error)	336 (88)	159 (28)
HHCB	Fitting formula	$Y = 1.6761 * \exp(-0.0231 * X)$	$Y = 23.9790 * \exp(-0.2491 * X)$
	R <sup>2</sup>	0.1762	0.6605
	p-value	0.0087	<0.0001
	k (error)	0.0231 (0.0078)	0.2491 (0.0381)
	t <sub>1/2</sub> (error)	900 (343)	83 (13)

<sup>a</sup> Correlation coefficient of the first-order reaction kinetic model.<sup>b</sup> Significance of the first-order reaction kinetic model.<sup>c</sup> Rate constant of the first-order reaction kinetic model.<sup>d</sup> The dissipation half-life (days) determined using the first-order reaction kinetic model under the two treatments (T1 and T2). It should be noted that the time unit is month in the kinetic equation.

repeated treatment of a compound to the same soil could saturate the sorption sites in the aggregates and increase the availability of this compound for the biodegradation (or extraction).

The dissipation of these four common personal care products in the biosolid-amended soils could be influenced by many factors such as environmental conditions (e.g. climate) and soil properties as well as physiochemical properties of the chemicals. These four chemicals (TCC, TCS, AHTN and HHCB) are hydrophobic compounds with high soil adsorption coefficients ( $K_{oc}$ ); therefore, leaching should be very limited (Butler et al., 2012; Litz et al., 2007; Wu et al., 2009). Biodegradation played a dominant role in the dissipation of these four chemicals in soils based on the laboratory degradation experiments under sterile and nonsterile conditions (Litz et al., 2007; Martin et al., 2007; Ying et al., 2007). Laboratory experiments by Ying et al. (2007) found that TCC and TCS were degraded in the aerobic soils with a half-life of 108 days and 18 days, but persisted in the anaerobic soils. Biosolid-borne TCC was found less bioavailable and degraded in biosolid-amended soils at a very low rate with <4% mineralization as measured by evolution of CO<sub>2</sub> over 7.5 months under aerobic conditions (Snyder et al., 2010b). In a one-year plot experiment on the three soils receiving sludge, less than 20% of the initial triclosan was recovered, and conversion into methyl-triclosan was observed (Butler et al., 2012). Under the field conditions of the present study, the half-lives (T1: 258 days; T2: 106 days) for TCS were higher than those for TCC (T1: 191 days; T2: 51 days). For AHTN and HHCB, a previous laboratory study showed a slow dissipation with 75% and 50% remaining in the biosolid-amended soils after 259 days (Litz et al., 2007). Consistent persistence for the four chemicals was found in the present study and previous studies,

while slight differences in their dissipation behaviors could be due to different environmental and experimental conditions, such as biosolid amendment and weather.

The presence of these four detected personal care products in the soils might pose potential risks to the soil ecosystem; therefore, a preliminary risk assessment was performed based on the limited terrestrial toxicity data available in the literature. As hydrophobic organic compounds, bioaccumulation has been reported in earthworms and plants (e.g., soybeans, lettuce and carrots) in some previous studies (Higgins et al., 2011; Litz et al., 2007; Wu et al., 2010). Accumulation of these personal care products in terrestrial animals and plants may impose toxic effects on these species themselves, and also pose potential risks to animals and humans who consume these plants (Wu et al., 2010). A previous study showed that TCS inhibited plant growth, with rice seeds being more sensitive than cucumber seeds with EC50 values of 57 and 108 mg/kg (Liu et al., 2009). The only terrestrial toxicity data for TCC was LC50 value (40 mg/kg) for the earthworms *Eisenia fetida* (Snyder et al., 2011), thus the calculated PNEC value for TCC was 40 µg/kg. Amorim et al. (2010) reported the terrestrial toxicity data for TCS to various invertebrates and plants with the lowest EC10 value of 0.6 mg/kg (*Eisenia andrei*), and proposed the PNEC value of 60 µg/kg for TCS. Based on the soil concentrations measured in the present study, high risks are expected for TCC in all three trial sites (both T1 and T2 at HN, SD and ZJ sites), but low to medium risks are expected for TCS in the three sites except for T2 at the HN site with high risks.

Previous studies also showed toxic effects of AHTN and HHCB on earthworms (*E. fetida*) and springtails (*Folsomia candida*) (Balk and Ford, 1999). The PNEC value for both AHTN and HHCB was proposed

**Table 5**

Predicted and measured concentrations (µg/kg) for the personal care products in biosolid-amended soils collected from the Shandong site.

Treatment	Biosolid application times	TCC		TCS		AHTN		HHCB	
		Predicted <sup>a</sup>	Measured <sup>b</sup>	Predicted	Measured	Predicted	Measured	Predicted	Measured
T1	1	805	365	80	6.5	32	3.6	68	1.0
T2	3	2415	1440	240	59.2	96	57.5	204	24.9

<sup>a</sup> The predicted concentrations were calculated using the measured concentrations of corresponding compounds in the biosolid. For both treatments (T1 and T2), the biosolid application rate is 60 t/ha per year. We assume that the plough depth is 20 cm and the soil bulk density is 1.3 g/cm<sup>3</sup>. We also presume that these compounds did not degrade within 3 years, so that we have the input concentrations for each compound.<sup>b</sup> The measured concentrations were determined in the biosolid-amended soils collected in October 2010.

to be 320 µg/kg (Balk and Ford, 1999). Low risks would be expected for AHTN and HHCB in the soils of T1 and T2 from the three trial sites (HN, SD and ZJ), except for HHCB in the soils of T2 in HN and ZJ with medium risks. In addition, additive effects might also be possible due to simultaneous exposure to multiple contaminants in biosolids. Thus further studies are required to understand the impact of these biosolid-associated contaminants on soil organisms.

## 5. Conclusion

The four typical personal care products (TCC, TCS, AHTN and HHCB) were detected in the biosolid-amended soils under two treatments (T1: single application; T2: repeated applications) at the three field trial sites (HN, SD and ZJ), with the following concentration order: TCC > TCS > AHTN > HHCB. The presence of these residual chemicals in the soils applied with biosolid indicates the persistence of these compounds in the soils. One-year field monitoring at the SD site showed dissipation of these chemicals with their half-lives of 51–900 days. Repeated applications of biosolid could lead to accumulation of these personal care products and result in higher ecological risks. Preliminary risk assessment suggests that TCC and TCS might pose high risks to soil organisms based on the limited toxicity data, while AHTN and HHCB showed low to medium ecological risks. Future studies should pay attention to the uptake of biosolid-associated chemicals by plants and potential risks to human health.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.10.080>.

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